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Bridged Tetraquaternary Salts from *N*,*N*′-Polyfluoroalkyl-4,4′-bipyridine

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4,4′-Bipyridine (**1**) with excess of polyfluoroalkyl bromide or iodides **2a**–**d** at 100–110 °C without solvent gave the monoquaternary salts **3a**–**d** in >90% yields. However, **1** with 2.5 equiv of **2a**–**c** in DMF at 110 °C resulted in the diquaternary salts **5a**–**c** in >85% yields. In DMF, **5a**–**c** were obtained in comparable yields when a molar excess of **2a**–**c** reacted with **3a**–**c.** 1,4-Dibromobutane with **3a,b** in DMF at 100 °C led to the tetraquaternary salts **7a,b** in ∼85% yields. In water or acetone/water as a solvent, salts **3a**–**d** and **5a**–**c** were metathesized with $LiN(SO_2CF_3)_2$ and KSO_3CF_3 to produce monoquaternary ionic liquids **4a**–**h** in >88% yields and diquaternary ionic liquids **6a**–**f** in >86% yields, respectively. Tetraquaternary ionic liquids **8a,b** were obtained when $LiN(SO_2CF_3)_2$ was reacted with salts **7a,b.** These compounds were stable to 340 °C as determined by DSC. They are the first *N*-mono-, *N*,*N*′-di-, and *N*,*N*,*N*′,*N*′-tetra-4,4′-polyfluoroalkylbipyridinium quaternary salts and ionic liquids.

Introduction

Polyquaternary salts of 4,4′-bipyridine are of considerable interest as demonstrated by the number of applications reported in the literature.[1] The simplest of these bis(4,4′-bipyridinium) salts are the so-called bis(viologen) compounds where two 4,4′-bipyridinium ions are joined by a varying number of methylene links to form tetraquaternary salts. Applications include reversible redox systems, photoinduced redox processes,[1b] bioelectronic mediators,[1c] components of redox active membranes,[2] chemical sensing,[3] and electrochromic memory display devices[4] as well as in melonoma cells as potent inhibitors of polyamine uptake and in emetics.[5]

The number and variety of 4,4′-dialkyl-substituted diquaternary and polyquatenary salts of 4,4′-bipridine are extensive.[6] Some of the diquaternary salts have been evaluated for antibacterial activity,[6b] for herbicidal properties,[6c,d] and for electron relays for the photoreduction of water.[6e] There are reports of a number of 2,2′-bipyridine compounds bearing various polyfluoroalkylated side chains with an ester or a methylene spacer in the 4,4′ positions.[7] Since quaternization of the *C*-polyfluoroalkylated bipyridines was not reported, the properties of such salts are unknown. However, it was demonstrated recently that the pyridine derivative 2,6-$NC_5H_3(CH_2CH_2C_8F_{17})_2$ can be quaternized with triflic acid to form a pyridinium triflate that is reported to exhibit a liquid crystalline phase that becomes an ionic liquid at high temperature (166.0/170.1 °C).[8] Several of these dipolyfluoroalkylated pyridines or bipyridines play a role in the catalytic aerobic oxidation of alcohols to aldehydes and ketones[7c,9] and epoxidation of *trans*-stilbene.[7b]

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While not the case for alkyl substitution, of the few reports dealing with polyfluoroalkyl substituents,[7−9] the latter are invariably bonded to carbon atom(s) of the pyridine or bipyridine ring. There are apparently few or no polyquaternary 4,4′-bipyridinium salts that have polyfluoroalkyl substituents at any ring position. Given the variety of applications of these poly salts, it is rather surprising that polyfluoroalkyl substituents have not been introduced to study the modifications in chemical and physical properties that invariably occur because of the presence of fluorine.

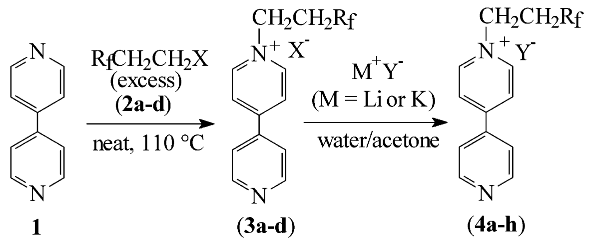
Here we report the high yield syntheses of the first *N*-mono- and *N*,*N*′-dipolyfluoroalkyl-4,4′-bipyridinium mono- and diquaternary salts that then can be linked subsequently to form the first fluoroalkyl-substituted tetraquaternary salts. Some of these salts with the appropriate anions fall into the ionic liquid class (MP < 100 °C) even when each of the fluorine-containing substituents is as large as C_8F_{17}.[10] This is often the case when the anion is the non-hydrogen bonding bis(trifluoromethanesulfonyl)amide. Moreover, comparison of the melting points of the dipolyfluoroalkylbipyridinium bis[bis(trifluoromethanesulfonyl)amide] with that of the reported dipolyfluoroalkylpyridinium triflate shows that in general the bipyridinium compounds with bis(trifluoromethanesulfonyl)amide anion melt lower. The yields of both the *N*-mono and *N*,*N*′-dipolyfluoro-substituted bipyridines are consistently higher than those obtained for the *C*-substituted pyridines.[8]

Results and Discussion

Bipyridines and their derivatives are important class of compounds in the field of organic and inorganic chemistry.[11] While a large numbers of studies have been reported involving nonfluorinated bipyridine compounds,[12] fluorinated analogues are studied more rarely.[8] Because of our interest in fluorine-containing quaternary salts,[13] we have studied the chemistry of 4,4′-bipyridines with various polyfluoroalkyl halides and the details of the chemistry is described here.

At the beginning of the project, 4,4′-bipyridine was contacted with an excess of polyfluoroalkyl halides at room temperature for several days but no reaction occurred.

Scheme 1



	Rf	X		Rf	X		Rf	Y	m.p (°C)
2a	CH_2F	Br	**3a**	CH_2F	Br	**4a**	CH_2F	$N(SO_2CF_3)_2$	62
2b	CF_3	I	**3b**	CF_3	I	**4b**	CF_3	$N(SO_2CF_3)_2$	67
2c	C_6F_{13}	I	**3c**	C_6F_{13}	I	**4c**	C_6F_{13}	$N(SO_2CF_3)_2$	52
2d	C_8F_{17}	I	**3d**	C_8F_{17}	I	**4d**	C_8F_{17}	$N(SO_2CF_3)_2$	94
						4e	CH_2F	SO_3CF_3	88
						4f	CF_3	SO_3CF_3	98
						4g	C_6F_{13}	SO_3CF_3	104
						4h	C_8F_{17}	SO_3CF_3	109

However, heating the neat mixture of 4,4′-bipyridine (**1**) with 1-bromo-3-fluoropropane (**2a**) at ∼100 °C for 24 h led to the formation of the monoquaternary salt (**3a**) as the only product that was insoluble in the excess polyfluoroalkyl halide. By removal of the unreacted excess **2a** in vacuo, **3a** remained in 95% yield. Under these reaction conditions, no diquaternary salt was formed. Using similar reaction conditions, **1** was reacted with other polyfluoroalkyl iodides (**2b**−**d**) to achieve the monoquaternary iodides (**3b**−**d**) in >90% yields (Scheme 1). In all of the reactions, excess polyfluoroalkyl halides were recovered by trapping at −195 °C in vacuo. It was found that higher temperatures were required for the *N*-alkylation of **1** with longer polyfluoroalkyl chains. The solubility of the monoquaternary salt in various solvents was found to be a function of the amount of fluorine present. For example, **3a**,**b** were soluble in acetone, water, and DMF whereas **3c** was only partially soluble in water but soluble in acetone and DMF. Compound **3d** was soluble in acetone and DMF but insoluble in water.

Monoquaternary salts (**3a**−**d**) were converted into ionic liquids (**4a**−**h**) by metathesizing with lithium bis(trifluoromethanesulfonyl)amide or potassium triflate using water or water/acetone reaction media (Scheme 1). Compounds **4a**−**h** are low melting salts and stable to water and air. They were soluble in acetone, ethyl acetate, and DMF but insoluble in hydrocarbons and water. Their thermal stabilities were determined by DSC, and no decomposition was found up to 340 °C.

Apparently, due to the insolubility of the monoquaternary salts in the liquid polyfluoroalkyl halides, diquaternary salts were not formed under neat conditions. However, if DMF was introduced as a solvent, diquaternary salts were obtained.

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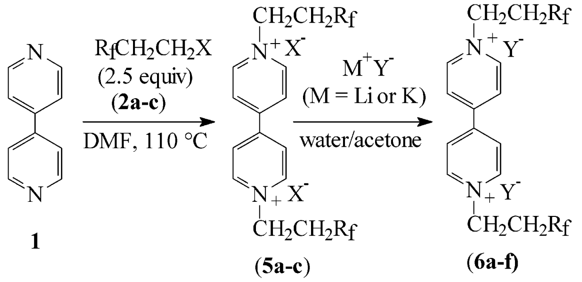
Scheme 2



	R_f	X		R_f	X		R_f	Y	m.p. (°C)
2a	CH_2F	Br	**5a**	CH_2F	Br	**6a**	CH_2F	$N(SO_2CF_3)_2$	64
2b	CF_3	I	**5b**	CF_3	I	**6b**	CF_3	$N(SO_2CF_3)_2$	96
2c	C_6F_{13}	I	**5c**	C_6F_{13}	I	**6c**	C_6F_{13}	$N(SO_2CF_3)_2$	149
						6d	CH_2F	SO_3CF_3	89
						6e	CF_3	SO_3CF_3	103
						6f	C_6F_{13}	SO_3CF_3	165

Thus, when reactions of **3a**−**c** with 1.25 equiv of **2a**−**c** were carried out in homogeneous solution of DMF at 110 °C, diquaternary salts **5a**−**c** were obtained after removing the solvent under reduced pressure. Alternatively, **5a**−**c** were also prepared in comparable yields using a single step reaction whereby a mixture of **1** was heated with 2.5 equiv of **2a**−**c** in DMF (Scheme 2). The diquaternary salt formed from reaction of **1** with 2. 5 equiv of $C_{10}F_{21}CH_2CH_2I$ were insoluble in all solvents tried. However, the composition was confirmed by elemental analysis to be $(C_{10}F_{21}CH_2CH_2)_2$(4,4′-bipyridinium)$^{2+}$$(I^-)_2$ (85% yield) . The diquaternary salts **5a**,**b** were soluble in water, DMF, and DMSO but insoluble in acetone. Compound **5c** was soluble in DMF and DMSO but insoluble in water and acetone. Metathetical reactions of **5a**−**c** with $LiN(SO_2CF_3)_2$ or KSO_3CF_3 gave the corresponding diquaternary compounds, **6a**−**f**, in good yields (Scheme 2). These compounds, **6a**−**f**, were soluble in acetone, ethyl acetate, DMF, and DMSO. They are thermally stable to 340 °C as determined by DSC.

The tetraquaternary salts, **7a**,**b**, where the two *N*-fluoropropyl- or *N*-trifluoropropyl-substituted bipyridine units are bridged with butyl ($-CH_2CH_2CH_2CH_2-$) were obtained from reaction of **3a** or **3b** with 0.5 equiv of 1,4-dibromobutane in DMF at 110 °C in good yields. These salts, **7a**,**b**, were insoluble in DMF but soluble in water. The metathesis of **7a**,**b** with $LiN(SO_2CF_3)_2$ in water gave the low melting salts (**8a,b)** in good yields (Scheme 3). These compounds were insoluble in water but soluble in acetone, ethyl acetate, and DMF. They are thermally stable to 340 °C and stable to air and water.

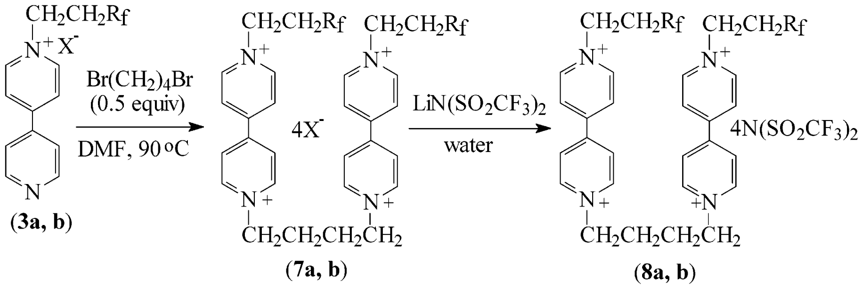
In conclusion, we report the synthesis of mono-, di-, and tetraquaternary salts of 4,4′-bipyridine that are N-substituted with polyfluorinated alkyl moieties. Depending on the reaction conditions employed either mono- or diquaternary salts can be obtained selectively. The monoquaternary compounds can be linked via an alkyl chain to give tetraquaternary salts. The metathesis reactions of the quaternary salts with $LiN(SO_2CF_3)_2$ or KSO_3CF_3 readily give products in high yields. Some of these meet the melting point criterion for ionic liquids.. All of the 4,4′-bipyridinium salts are stable to water and air and were thermally stable up to 340 °C as determined by DSC. They are generally soluble in acetone, ethyl acetate, DMF, and DMSO. The polyfluoroalkylated mono-, di-, and tetraquaternary 4,4′-bipyridinium salts are likely to have a considerable practical chemistry. We shall report our progress in that area as the work develops.

Experimental Section

General Methods. All the reagents used were analytical reagents. Bipyridine and fluorinated or polyfluorinated alkyl halides, $LiN(SO_2CF_3)_2$, and KSO_3CF_3 were purchased from commercial sources and used as received. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded in acetone-d_6 unless otherwise specified on a spectrometer operating at 300, 282, and 75 MHz, respectively. Chemical shifts are reported in ppm relative to the appropriate standard, $CFCl_3$ for ^{19}F and TMS for ^1H and ^{13}C NMR spectra. IR spectra were recorded using NaCl plates for neat liquids and KBr pellets for solids. DSC data were recorded in the range of −85 to 400 °C. Elemental analyses were carried out at the Shanghai Institute for Organic Chemistry.

General Procedure for the Synthesis of 3a−d and 4a−h. 2,2′-Bipyridine (**1**) (2 mmol) and $R_fCH_2CH_2I$ (**2a**−**d**) (5 mmoL) were

Scheme 3



	R_f	X		R_f	X		R_f	m.p (°C)
3a	CH_2F	Br	**7a**	CH_2F	Br	**8a**	CH_2F	121
3b	CF_3	I	**7b**	CF_3	I	**8b**	CF_3	125

mixed at room temperature in a 50 mL Schlenk tube. After the sample was cooled to −195 °C, the tube was evacuated and closed. The reaction mixture was heated at 110 °C for 24 h. The monoquaternary salt is insoluble in the excess $R_fCH_2CH_2I$. The latter was recovered by removing in vacuo. Mono quaternary salts with $R_f = CH_2F$, CF_3, C_4F_9, and C_6F_{13} (**3a**−**c**) were obtained analytically pure whereas **3d** ($R_f = C_8F_{17}$) was purified by crystallization from acetone. These salts, **3a**−**d** were dissolved in a mixture of water and acetone (1:0.5) and treated with 1.25 equiv aqueous solution of $LiN(SO_2CF_3)_2$ or KSO_3CF_3. After 6 h, acetone was removed at reduced pressure and the insoluble products (**4a**−**h**) were separated by filtration from water.

3a: yield, 95%; IR (KBr pellet) 3032, 1641, 1598, 1546, 1465, 1412, 1173, 1038, 928, 816, cm^{-1}; ^{19}F NMR δ −222.88 (tt, 1F, J = 50.5 Hz, J = 28.2 Hz); ^{1}H NMR δ 2.44 (ttd, 2H, J = 26.5 Hz, J = 5.5 Hz, J = 2.5 Hz), 4.59 (t, 1H, J = 5.2 Hz), 4.68 (t, 1H, J = 5.2 Hz), 4.88 (t, 2H, J = 7.1 Hz), 7.85 (d, 2H, J = 4.4 Hz), 8.42 (d, 2H, J = 6.8 Hz), 8.83 (d, 2H, J = 4.4 Hz), 9.16 (d, 2H, J = 6.8 Hz); ^{13}C NMR δ 31.5 (d, J = 19.3 Hz), 58.1, 81.1 (d, J = 162.0 Hz), 117.3, 121.9, 126.0, 141.2, 145.5, 151.1. Anal. Calcd for $C_{13}H_{14}BrFN_2$: C, 52.54; H, 4.75. Found: C, 52.40; H, 4.74.

3b: yield, 95%; IR (KBr pellet) 3013, 1643, 1598, 1546, 1411, 1292, 1165, 1136, 997, 877, 816, 720 cm^{-1}; ^{19}F NMR δ −60.43 (t, 3F, J = 7.8 Hz); ^{1}H NMR δ 3.09 (m, 2H), 4.95 (t, 1H, J = 7.0 Hz), 7.84 (d, 2H, J = 4.4 Hz), 8.42 (d, 2H, J = 6.8 Hz), 8.84 (d, 2H, J = 4.4 Hz), 9.06 (d, 2H, J = 6.8 Hz); ^{13}C NMR δ 34.4 (q, J = 29.5 Hz), 54.5, 121.6, 125.5 (q, J = 274.2 Hz), 126.2, 141.1, 146.2, 151.3, 155.1. Anal. Calcd for $C_{13}H_{12}F_3IN_2$: C, 41.07; H, 3.18. Found: C, 41.37; H, 3.30.

3c: yield, 92%; IR (KBr pellet) 3015, 1645, 1587, 1550, 1418, 1299, 1158, 982, 873, 823, 715 cm^{-1}; ^{19}F NMR δ −76.94 (t, 3F, J = 8.6 Hz), −108.85 (m, 2F), −117.63 (m, 2F), −118.69 (m, 2F), −119.15 (m, 2F), −122.03 (m, 2F); ^{1}H NMR δ 3.46 (tt, 2H, J = 11.5 Hz, J = 7.0 Hz), 8.07 (d, 2H, J = 4.5 Hz), 8.82 (d, 2H, J = 6.9 Hz), 8.87 (d, 2H, J = 4.5 Hz), 9.72 (d, 2H, J = 6.9 Hz); ^{13}C NMR δ 31.7 (t, J = 21.3 Hz), 53.3, 110−123.0 (overlapped quartets with multiplets), 121.9, 126.0, 141.0, 146.3, 151.2, 154.5. Anal. Calcd for $C_{18}H_{12}F_{13}IN_2$: C, 34.30; H, 1.92. Found: C, 34.22; H, 2.13.

3d: yield, 90%; IR (KBr pellet) 3024, 1639, 1595, 1544, 1409, 1200, 1147, 1074, 955, 810, 704, 660 cm^{-1}; ^{19}F NMR δ −82.07 (t, 3F, J = 9.5 Hz), −113.96 (m, 2F), −112.49 (m, 2F), −122.79 (m, 4F), −123.62 (m, 2F), −124.23 (m, 2F), 127.10 (m, 2F); ^{1}H NMR δ 3.52 (tt, 2H, J = 11.6 Hz, J = 7.2 Hz), 5.38 (t, 2H, J = 7.2 Hz), 8.10 (d, 2H, J = 7.3 Hz), 8.81 (d, 2H, J = 6.6 Hz), 8.98 (d, 2H, J = 7.5 Hz), 9.76 (d, 2H, J = 6.6 Hz); ^{13}C NMR δ 32.5 (t, J = 23.0 Hz), 54.2, 110−123.0 (overlapped quartets with multiplets), 122.6, 126.8, 141.9, 147.1, 152.1, 155.5. Anal. Calcd for $C_{20}H_{12}F_{17}IN_2$: C, 32.90; H, 1.66. Found: C, 32.74; H, 1.74.

4a: yield, 89%; IR (KBr pellet) 3073, 1600, 1547, 1523, 1466, 1412, 1351, 1199, 1137, 1056, 866, 814, 789, 738, cm^{-1}; ^{19}F NMR δ −75.11 (s, 6F), −217.74 (tt, 1F, J = 50.5 Hz, J = 28.2 Hz); ^{1}H NMR δ 2.65 (ttd, 2H, J = 26.5 Hz, J = 5.5 Hz, J = 2.5 Hz), 4.70 (t, 2H, J = 5.5), 5.06 (t, 2H, J = 7.1 Hz), 7.99 (d, 2H, J = 4.4 Hz), 8.67 (d, 2H, J = 6.8 Hz), 8.87 (d, 2H, J = 4.4 Hz), 9.33 (d, 2H, J = 6.8 Hz); ^{13}C NMR δ 31.62 (d, J = 19.6 Hz), 58.7, 80.9 (d, J = 162.7 Hz), 120.1 (q, J = 319.3), 121.8, 126.1, 141.2, 145.7, 151.2, 153.3. Anal. Calcd for $C_{15}H_{14}F_7N_3O_2S_4$: C, 36.22; H, 2.84. Found: C, 36.28; H, 2.90.

4b: yield, 90%; IR (KBr pellet) 3072, 1644, 1602, 1548, 1525, 1467, 1350, 1190, 1137, 1055, 963, 918, 815, 790, 738 cm^{-1}; ^{19}F NMR δ −60.66 (t, 3F, J = 9.3 Hz), −75.1 (s, 6F); ^{1}H NMR δ 3.36 (tq, 2H, J = 10.5 Hz, J = 7.2 Hz), 5.27 (t, 2, J = 7.2 Hz), 8.00 (d, 2H, J = 4.5 Hz), 8.74 (d, 2H, J = 6.7 Hz), 8.88 (d, 2H, J = 4.5 Hz), 9.43 (d, 2H, J = 6.7 Hz); ^{13}C NMR δ 34.2 (q, J = 29.6 Hz), 54.7, 120.14 (q, J = 319.8 Hz), 121.8, (125.8 (q, J = 274.6 Hz), 126.2, 141.0, 146.0, 151.3, 155.0. Anal. Calcd for $C_{15}H_{12}F_9N_3O_4S_2$: C, 33.78; H, 2.27. Found: C, 33.77; H, 2.35.

4c: yield, 88%; IR (KBr pellet) 3075, 1644, 1602, 1549, 1525, 1495, 1467, 1411, 1349, 1193, 1057, 965, 870, 815, 791, 740 cm^{-1}; ^{19}F NMR δ −80.35 (s, 6F), −82.16 (tt, 3F, J = 9.5 Hz, J = 2.3 Hz), −114.19 (m, 2F), −122.78 (m, 2F), −123.82 (m, 2F), −124.43 (m, 2F), 127.18 (m, 2F); ^{1}H NMR δ 3.39 (ttt, 2H, J = 11.5 Hz, J = 7.1 Hz, J = 2.5 Hz), 5.37 (t, 2H, J = 7.2 Hz), 8.02 (s, broad, 2H), 8.74 (d, 2H, J = 6.7 Hz), 8.91 (s, broad, 2H), 9.47 (d, 2H, J = 6.7 Hz); ^{13}C NMR δ 31.5 (t, J = 20.8 Hz), 53.6, 110−122 (overlapped quartets with multiplets), 126.2, 141.1, 146.2, 151.2, 151.5, 155.0. Anal. Calcd for $C_{20}H_{12}\ F_{19}N_3O_4S_2$: C, 30.70; H, 1.54. Found: C, 30.61; H, 1.79.

4d: yield, 88%; IR (KBr pellet) 3070, 1645, 1602, 1549, 1469, 1414, 1250, 1211, 1150, 1033, 962, 835, 704, 656 cm^{-1}; ^{19}F NMR δ −75.16 (s, 6F), −76.87 (tt, 3F, J = 9.5 Hz, J = 2.3 Hz), −109.00 (m, 2F), −117.44 (m, 2F), −117.71 (m, 4F), −118.55 (m, 2F), 119.10 (m, 2F), 122.01 (m, 2F); ^{1}H NMR δ 3.31 (tt, 2H, J = 11.6 Hz, J = 7.2 Hz), 5.27 (t, 2H, J = 7.2 Hz), 8.01 (d, 2H, J = 7.3 Hz), 8.66 (d, 2H, J = 6.8 Hz), 8.55 (d, 2H, J = 7.4 Hz), 9.38 (d, 2H, J = 6.7 Hz); ^{13}C NMR δ 32.1 (q, J = 22.5 Hz), 54.2, 110−122 (overlapped quartets with multiplets), 123.0, 126.9, 142.3, 146.7, 146.8, 151.5, 155.3. Anal. Calcd for $C_{22}H_{12}\ F_{23}N_3O_4S_2$: C, 29.90; H, 1.37. Found: C, 30.00; H, 1.58.

4e: yield, 88%; IR (KBr pellet) 3066, 1644, 1603, 1547, 1525, 1466, 1332, 1255, 1225, 1163, 1029, 869, 754, 726 cm^{-1}; ^{19}F NMR δ −74.21 (s, 3F), −217.63 (tt, 1F, J = 48.0 Hz, J = 25.3 Hz); ^{1}H NMR δ 2.53 (ttd, 2H, J = 26.4 Hz, J = 5.4 Hz, J = 2.5 Hz), 4.72 (td, 2H, J = 48.0, J = 5.5), 5.06 (t, 2H, J = 7.2 Hz), 8.03 (d, 2H, J = 4.5 Hz), 8.68 (d, 2H, J = 6.8 Hz), 8.87 (d, 2H, J = 4.5 Hz), 9.35 (d, 2H, J = 6.8 Hz); ^{13}C NMR δ 32.64 (d, J = 19.6 Hz), 59.4, 81.8 (d, J = 162.5 Hz), 122.1 (q, J = 319.3), 122.6, 126.8, 142.1, 146.6, 152.0, 154.9. Anal. Calcd for $C_{14}H_{14}F_4N_2O_3S$: C, 45.90; H, 3.85. Found: C, 45.87; H, 3.86.

4f: yield, 87%; IR (KBr pellet) 3070, 1636, 1603, 1543, 1517, 1472, 1351, 1192, 1132, 1054, 963, 915, 812, 787, 736 cm^{-1}; ^{19}F NMR δ −60.65 (t, 3F, J = 9.3 Hz), −74.20 (s, 3F); ^{1}H NMR δ 3.34 (tq, 2H, J = 10.6 Hz, J = 7.0 Hz), 5.27 (t, 2, J = 7.7 Hz), 8.01 (d, 2H, J = 4.5 Hz), 8.76 (d, 2H, J = 6.6 Hz), 8.85 (d, 2H, J = 4.5 Hz), 9.43 (d, 2H, J = 6.7 Hz); ^{13}C NMR δ 34.0 (q, J = 29.5 Hz), 54.6, 121.5 (q, J = 319.5 Hz), 121.8, 125.4 (q, J = 274.5 Hz), 126.2, 141.0, 146.0, 151.3, 155.0. Anal. Calcd for $C_{14}H_{12}F_6N_2O_3S$: C, 41.80; H, 3.01. Found: C, 40.71; H, 3.19.

4g: yield, 88%; IR (KBr pellet) 3065, 1645, 1608, 1554, 1522, 1486, 1418, 1342, 1195, 1058, 972, 868, 814, 786, 736 cm^{-1}; ^{19}F NMR δ −74.30 (s, 3F), −76.94 (tt, 3F, J = 9.5 Hz, J = 2.2 Hz), −109.0 (m, 2F), −117.7 (m, 2F), −118.6 (m, 2F), −119.2 (m, 2F), 122.06 (m, 2F); ^{1}H NMR δ 3.41 (ttt, 2H, J = 11.4 Hz, J = 7.2 Hz, J = 2.5 Hz), 5.36 (t, 2H, J = 7.2 Hz), 8.04 (d, 2H, J = 4.5 Hz), 8.75 (d, 2H, J = 6.8 Hz), 8.89 (d, 2H, J = 4.5 Hz), 9.48 (d, 2H, J = 6.7 Hz); ^{13}C NMR δ 32.3 (t, J = 22.2 Hz), 54.3, 110−122 (overlapped quartets with multiplets),122.6, 126.9, 141.9, 147.1, 152.0, 155.5. Anal. Calcd for $C_{19}H_{12}\ F6_6N_2O_3S$: C, 34.98; H, 1.85. Found: C, 35.13; H, 1.74.

4h: yield, 88%; IR (KBr pellet) 3066, 1645, 1548, 1465, 1415, 1259, 1169, 1031, 817, 705, 639 cm^{-1}; ^{19}F NMR δ −74.33 (s, 3F), −76.95 (tt, 3F, J = 9.5 Hz, J = 2.3 Hz), −109.50 (m, 2F), −118.12 (m, 4F), −118.42 (m, 2F), −119.56 (m, 2F), 119.10 (m, 2F), 122.00 (m, 2F); ^{1}H NMR: δ 3.37 (tt, 2H, J = 11.5 Hz, J = 7.1 Hz), 5.32 (t, 2H, J = 7.1 Hz), 8.04 (d, 2H, J = 7.2 Hz), 8.71

(d, 2H, $J = 6.4$ Hz), 8.87 (d, 2H), 9.44 (d, 2H, $J = 6.5$ Hz); ^{13}C NMR δ 30.6 (t, $J = 21.5$ Hz), 54.3, 110−123 (overlapped quartets with multiplets), 122.8, 126.9, 142.2, 147.1, 151.9, 155.3. Anal. Calcd for $C_{21}H_{12}F_{20}N_2O_3S$: C, 33.51; H, 1.63. Found: C, 33.42; H, 1.72.

Syntheses of 5a−c and 6a−f. The procedure was as for **3a−d** except that DMF was used as solvent, e.g., **3a−c** (2 mmol) with 1.25 equiv of pressure. Alternatively, heating 1 (2 mmol) with 2.5 equiv of **2a−c** in DMF gives comparable yields of **5a−c**. The salts, **5a−c**, were dissolved in a mixture of water and acetone (1:0.5) and treated with 1.25 equiv of an aqueous solution of either $LiN(SO_2CF_3)_2$ or $KS0_3CF_3$. The corresponding diquaternary compounds, **6a−f**, were recovered as above.

5a: yield, 91%; IR (KBr pellet) 2978, 1639, 1561, 1507, 1450, 1393, 1350, 1224, 1176, 1037, 1000, 919, 838, 788, cm^{-1}; ^{19}F NMR δ −220.98 (tt, 2F, $J = 50.6$ Hz, $J = 28.2$ Hz); ^{1}H NMR δ 2.57 (ttd, 2H, $J = 26.5$ Hz, $J = 5.5$ Hz, $J = 2.5$ Hz), 4.63 (t, 2H, $J = 5.2$ Hz), 4.78 (t, 2H, $J = 5.2$ Hz), 4.95 (t, 4H, $J = 7.0$ Hz), 8.62 (d, 4H, $J = 5.3$ Hz), 9.21 (d, 4H, $J = 5.5$ Hz); ^{13}C NMR δ 32.0 (d, $J = 19.3$ Hz), 60.0, 82.4 (d, $J = 160.0$ Hz), 128.1, 146.7, 151.2. Anal. Calcd for $C_{16}H_{20}Br_2F_2N_2$: C, 43.86; H, 4.60. Found: C, 43.87; H, 4.61.

5b: yield, 90%; IR (KBr pellet) 2959, 1641, 1508, 1448, 1255, 1176, 1143, 997, 966, 870, 830, 728 cm^{-1}; ^{19}F NMR δ −65.10 (t, 6F, $J = 10.3$ Hz); ^{1}H NMR δ 3.15 (tt, 4H, $J = 7.1$ Hz, $J = 3.4$ Hz), 5.07 (t, 4H, $J = 7.2$ Hz), 8.60 (d, 4H, $J = 6.8$ Hz), 9.63 (d, 4H, $J = 6.8$ Hz); ^{13}C NMR δ 34.89 (t, $J = 29.6$ Hz), 56.0, 126.2 (q, $J = 274.8$ Hz), 128.3, 146.9, 151.5. Anal. Calcd for $C_{16}H_{16}F_6I_2N_2$: C, 31.81; H, 2.67. Found: C, 31.80; H, 2.70.

5c: yield, 89%; IR (KBr pellet) 3072, 1641, 1565, 1502, 1400, 1350, 1222, 1050, 1005, 967, 838, 790, 736 cm^{-1}; ^{19}F NMR δ −80.32 (tt, 6F, $J = 11.2$ Hz), −112.46 (m, 4F), −121.64 (m, 4F), −122.62 (m, 4F), −123.10 (m, 4), −125.76 (m, 4F); ^{1}H NMR δ 3.30 (tt, 4H, $J = 7.4$ Hz, $J = 3.4$ Hz), 5.13 (t, 4H, $J = 7.3$ Hz), 8.90 (d, 4H, $J = 7.0$ Hz), 9.54 (d, 4H, $J = 7.0$ Hz); ^{13}C NMR δ 32.4 (t, $J = 22.0$ Hz), 54.8, 110−123 (overlapped quartets with multiplets), 129.6, 146.4, 147.7. Anal. Calcd for $C_{26}H_{16}F_{26}I_2N_2$: C, 28.30; H,1.50. Found: C, 28.20; H, 1.27.

6a: yield, 90%; IR (KBr pellet) 2978, 1643, 1562, 108, 1454, 1254, 1186, 1050, 918, 836, 791, cm^{-1}; ^{19}F NMR δ −79.81 (s, 12F), −222.47 (tt, 2F, $J = 67.5$ Hz, $J = 25.4$ Hz); ^{1}H NMR δ 2.65 (ttd, 2H, $J = 26.5$ Hz, $J = 5.5$ Hz, $J = 2.5$ Hz), 4.64 (t, 2H, $J = 5.5$ Hz), 4.80 (t, 2H, $J = 5.5$ Hz), 5.12 (t, 4H, $J = 7.0$ Hz), 8.84 (d, 4H, $J = 7.0$ Hz), 9.45 (d, 4H, $J = 7.0$ Hz); ^{13}C NMR: δ 32.4 (d, $J = 19.6$ Hz), 60.2, 81.7 (d, $J = 162.7$ Hz), 118.7 (q, $J = 319.2$ Hz), 128.2, 147.1, 151.5. Anal. Calcd for $C_{20}H_{20}F_{14}N_4O_8S_4$: C, 28.64; H, 2.40. Found: C, 28.61; H, 2.41.

6b: yield, 92%; IR (KBr pellet) 3076, 1641, 1561, 1508, 1458, 1405, 1343, 1228, 1058, 1005, 971, 873, 831, 791, 734 cm^{-1}; ^{19}F NMR δ −65.38 (t, 6F, $J = 10.4$ Hz), −79.85 (s, 6F); ^{1}H NMR δ 3.39 (tt, 4H, $J = 7.2$ Hz, $J = 3.5$ Hz), 5.37 (t, 4H, $J = 7.2$ Hz), 8.97 (d, 4H, $J = 6.9$ Hz), 9.63 (d, 4H, $J = 6.9$ Hz); ^{13}C NMR δ 35.0 (t, $J = 29.8$ Hz), 56.1, 121.0 (q, $J = 319.9$ Hz), 126.7 (q, $J = 275.1$), 128.4, 147.6, 151.5. Anal. Calcd for $C_{20}H_{16}F_{18}N_4O_8S_4$: C, 26.38; H,1.77. Found: C, 26.30; H, 1.80.

6c: yield, 88%; IR (KBr pellet) 3073, 1640, 1561, 1508, 1448, 1365, 1335, 1238, 1197, 1139, 1076, 1053, 963, 869, 738 cm^{-1}; ^{19}F NMR δ −80.39 (s, 12F), −82.16 (tt, 6F, $J = 11.2$ Hz, 3.7 Hz), −114.13 (m, 4F), −122.78 (m, 4F), −123.83 (m, 4F), −124.43 (m, 4), −127.22 (m, 4F); ^{1}H NMR δ 3.39 (tt, 4H, $J = 7.5$ Hz, $J = 3.5$ Hz), 5.43 (t, 4H, $J = 7.3$ Hz), 8.92 (d, 4H, $J = 7.0$ Hz), 9.64 (d, 4H, $J = 7.0$ Hz); ^{13}C NMR δ 32.4 (t, $J = 21.5$ Hz), 55.1, 110−123 (overlapped quartets with multiplets), 128.4, 147.7, 151.5. Anal. Calcd for $C_{30}H_{16}F_{38}N_4O_8S_4$: C, 25.54; H, 1.14. Found: C, 25.51; H, 1.12.

6d: yield, 85%; IR (KBr pellet) 3070, 1637, 1560, 1508, 1449, 1369, 1185, 1144, 1093, 1073, 910, 834, 759 cm^{-1}; ^{19}F NMR δ −79.03 (s, 6F), −222.27 (tt, 2F, $J = 67.6$ Hz, $J = 25.3$ Hz); ^{1}H NMR δ 2.65 (ttd, 2H, $J = 26.5$ Hz, $J = 5.5$ Hz, $J = 2.5$ Hz), 4.80 (t, 2H, $J = 5.5$ Hz), (t, 4H, $J = 7.1$ Hz), 8.86 (d, 4H, $J = 6.68.0$ Hz), 9.46 (d, 4H, $J = 6.8$ Hz); ^{13}C NMR δ 32.1 (d, $J = 19.3$ Hz), 60.0, 82.2 (d, $J = 160.0$ Hz), 122.3 (q, $J = 319.3$), 128.0, 146.5, 151.2. Anal. Calcd for $C_{18}H_{20}F_8N_2O_6S_2$: C, 37.50; H, 3.50. Found: C, 37.28; H, 3.44.

6e: yield, 86%; IR (KBr pellet) 3066, 1645, 1548, 1465, 1415, 1259, 1169, 1031, 817, 705 cm^{-1}; ^{19}F NMR δ ∠65.34 (t, 6F, $J = 10.5$ Hz), −78.97 (s, 6F); ^{1}H NMR δ 3.40 (tt, 4H, $J = 7.2$ Hz, $J = 3.5$ Hz), 5.34 (t, 4H, $J = 7.2$ Hz), 8.95 (d, 4H, $J = 7.0$ Hz), 9.57 (d, 4H, $J = 7.0$ Hz); ^{13}C NMR δ 35.0 (t, $J = 29.7$ Hz), 55.9, 120.5 (q, $J = 318.5$ Hz), 126.7 (q, $J = 276.0$), 128.4, 147.6, 151.4. Anal. Calcd for $C_{18}H_{16}F_{12}N_2O_6S_2$: C, 33.30; H, 2.50. Found: C, 33.20; H, 2.54.

6f: yield, 86%; IR (KBr pellet) 3075, 1639, 1564, 1500, 1405, 1345, 1220, 1051, 1005, 969, 831, 791, 733 cm^{-1}; ^{19}F NMR δ −78.99 (s, 6F), −81.64 (tt, 6F, $J = 11.2$ Hz), −113.65 (m, 4F), −122.31 (m, 4F), −123.37 (m, 4F), −123.92 (m, 4), −126.75 (m, 4F); ^{1}H NMR δ 3.43 (tt, 4H, $J = 7.5$ Hz, $J = 3.5$ Hz), 5.47 (t, 4H, $J = 7.3$ Hz), 8.98 (d, 4H, $J = 6.9$ Hz), 9.70 (d, 4H, $J = 6.9$ Hz); ^{13}C NMR: δ 32.3 (t, $J = 21.5$ Hz), 54.9, 110−123 (overlapped quartets with multiplets), 128.4, 147.7, 151.4. Anal. Calcd for $C_{28}H_{16}F_{32}N_2O_6S_2$: C, 29.28; H,1.40. Found: C, 29.30; H, 1.38.

Syntheses of 7a,b and 8a,b. Compounds **3a−b** (2 mmol) were reacted with 0.5 equiv of 1,4-dibromobutane in DMF at 110 °C to obtain good yields of **7a,b**. The latter were solubilized in water and reacted with a 1.25 equiv of $LiN(SO_2CF_3)_2$ to form the water-insoluble salts in good yields.

7a: yield, 94%; IR (KBr pellet) 3034, 1638, 1660, 1508, 1450, 1353, 1179, 1037, 918, 830 cm^{-1}; ^{19}F NMR (D_2O) δ −219.08 (tt, 2F, $J = 56.5$ Hz, $J = 28.2$ Hz); ^{1}H NMR (D_2O) δ 2.30 (t, 4H, $J = 7$ Hz), 2,55 (ttd, 2H, $J = 26.5$ Hz, $J = 5.5$ Hz, $J = 2.5$ Hz), 4.65 (t, 2H, $J = 5.3$ Hz), 4.74 (t, 2H, $J = 5.3$ Hz), 4.87 (t, 4H, $J = 7$ Hz), 4.94 (t, 4H, $J = 7.0$ Hz), 8.62 (d, 8H, $J = 7.0$ Hz), 9.19 (d, 4H, $J = 4.5$ Hz), 9.21 (d, 4H, $J = 4.5$ Hz); ^{13}C NMR (D_2O) δ 28.3, 32.1 (d, $J = 19.3$ Hz), 60.0, 62.0, 82.5 (d, $J = 160.0$ Hz), 128.2, 128.3, 146.5, 146.7, 151.1, 151.2 Anal. Calcd for $C_{30}H_{36}Br_4F_2N_4$: C, 44.97; H, 4.48. Found: C, 44.24; H, 4.51.

7b: yield, 95%; IR (KBr pellet) 3035, 1639, 1562, 1509, 1452, 1400, 1351, 1288, 1257, 1174, 1147, 1109, 1002, 967, 836, 716 cm^{-1}; ^{19}F NMR (D_2O) δ −62.51 (t, 6F, $J = 10.0$ Hz); ^{1}H NMR (D_2O) δ 2.34 (t, 4H, $J = 7$ Hz), 3.23 (tt, 4H, $J = 7.1$ Hz, $J = 3.5$ Hz), 4.91 (t, 4H, $J = 7$ Hz), 5.15 (t, 4H, $J = 7.0$ Hz), 8.65 (d, 4H, $J = 6.7$ Hz), 8.68 (d, 4H, $J = 6.5$ Hz), 9.24 (d, 4H, $J = 6.5$ Hz), 9.30 (d, 4H, $J = 6.5$ Hz); ^{13}C NMR (D_2O) δ 27.5, 34.2 (t, $J = 29.6$ Hz), 55.2, 61.3, 125.5 (q, $J = 275.0$), 127.6, 145.8, 146.2, 150.1, 151.0. Anal. Calcd for $C_{30}H_{32}Br_2F_6I_2N_4$: C, 36.91; H, 3.30. Found: C, 36.68; H, 3.39.

8a: yield, 82%; IR (KBr pellet) 2032, 1638, 1560, 1506, 1449, 1356, 1175, 1132, 1058, 922, 873, 830, 790, 738 cm^{-1}; ^{19}F NMR δ −75.11 (s, 24F), −217.08 (tt, 2F, $J = 56.4$ Hz, $J = 28.2$ Hz); ^{1}H NMR (D_2O) δ 2.50 (t, 4H, $J = 7$ Hz), 2.66 (ttd, 2H, $J = 26.5$ Hz, $J = 5.5$ Hz, $J = 2.5$ Hz), 4.64 (t, 2H, $J = 5.4$ Hz), 4.80 (t, 2H, $J = 5.4$ Hz), 5.10 (t, 4H, $J = 7$ Hz), 5.14 (t, 4H, $J = 7.1$ Hz), 8.83 (d, 8H, $J = 5.5$ Hz), 9.40 (d, 4H, $J = 7.0$ Hz), 9.50 (d, 4H, $J = 7.0$ Hz); ^{13}C NMR (D_2O) δ 28.6, 32.4 (d, $J = 19.6$ Hz), 60.2, 62.2, 81.7 (d, $J = 160.0$ Hz), 120.8 (q, $J = 319.3$ Hz), 128.2, 128.3, 146.9, 147.1, 151.0, 151.1. Anal. Calcd for $C_{38}H_{36}F_{26}N_8O_{16}S_8$: C, 28.33; H, 2.25. Found: C, 28.24; H, 2.32.

8b: yield, 95%; IR (KBr pellet) 3073, 1639, 1565, 1507, 1438, 1398, 1285, 1195, 1135, 1054, 972, 831, 792, 741 cm^{-1}; ^{19}F NMR (D_2O) δ -63.20 (t, 6F, $J = 10.0$ Hz); ^1H NMR (D_2O) δ 2.51 (t, 4H, $J = 7$ Hz), 3.39 (tt, 4H, $J = 7.1$, Hz, $J = 3.5$ Hz), 5.11 (t, 4H, $J = 7$ Hz), 5.36 (t, 4H, $J = 7.1$ Hz), 8.86 (d, 4H, $J = 6.7$ Hz), 8.90 (d, 4H, $J = 6.5$ Hz), 9.42 (d, 4H, $J = 6.5$ Hz), 9.61 (d, 4H, $J = 6.5$ Hz); ^{13}C NMR δ 27.8, 34.4 (t, $J = 29.6$ Hz), 55.3, 61.6, 120.5 (q, $J = 319.4$ Hz), 125.8 (q, $J = 275.0$), 127.8, 145.5, 146.4, 150.2, 151.3. Anal. Calcd for $C_{38}H_{32}F_{30}N_8O_{16}S_8$: C, 27.12; H, 1.92. Found: C, 27.00; H, 2.10.

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